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Bioremediation of oily sludge at HPCL Refinery, Visakhapatnam

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For more information about this report, please contact

Microbial Biotechnology
T E R I
Darbari Seth Block
Habitat Place, Lodhi Road
New Delhi – 110 003 / India

Telephone +91 11 468 2111 or 468 2100
E-mail mailbox@teri.res.in
Fax +91 11 468 2144 or 468 2145
Web site www.teriin.org

Project Team

Team Members

Dr. Banwari Lal (Principal Investigator)

Mr. Vinod Kumar

Mr. Abu Swaleha

Mr. Samarjeet

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(Banwari Lal, Vinod Kumar, Abu Swaleya and Samarjeet)

1 Introduction

Petroleum refineries occupy a key role in the economy of our country. Presently, there are 14 oil refineries of various sizes operating in India. These oil refineries generate huge volume of oily sludge. Management of oily sludge is one of the major problems being faced by the refineries.

Oily sludge is hazardous waste which causes enormous environmental pollution. According to the existing classification of hazardous waste, the refinery oily sludge falls under Hazardous Waste Category no. 10 and 12. Due to stringent norms by regulatory authority and corporate responsibility of oily refinery to protect environment, new techniques are continuously in demand in India to manage oily sludge. However, in developed countries, new technologies are continuously being invented and implemented for treatment of oily sludge. Several technologies, which were considered emerging a few years back are now well known and accepted in the field of hazardous waste treatment. One such technology is the bioremediation of oily sludge using specialised bacteria. These specialised bacteria have the capability to breakdown and digest oily sludge and convert them into harmless products like carbon dioxide, water and fatty acids.

As a timely response to the increasing importance of such microorganisms that efficiently biodegrade and detoxify oily sludge, TERI has developed a bacterial consortium known as Oilzapper. Oilzapper is a mixture of five natural occurring bacterial strains, which can biodegrade all the fractions of oily sludge at very fast rate. Oilzapper is being used for bioremediation of oily sludge by Indian Oil Corporation Ltd., Bharat Petroleum Corporation Ltd., Hindustan Petroleum Corporation Ltd., Oil & Natural Gas Corporation Ltd. and Oil India Ltd.

2 Methods

Selection of site for bioremediation of oily sludge

Oily sludge bioremediation site was selected in new tank farm area situated outside the refinery campus. A pit (size 30 m x 20 m) which was having approximately 350 metric tonnes of oily sludge was selected for bioremediation. Initially in the month of May 2000, first dose of Oilzapper (200 kg) and 200 litres of nutrients were applied on oily sludge. Tilling of sludge was carried out using JCB for uniform mixing of Oilzapper bacterial cells in sludge (Figure 1). Oily sludge samples collected at time zero, after two, four, six and nine months from the treatment pit were transported to TERI laboratory at New Delhi for analysis.

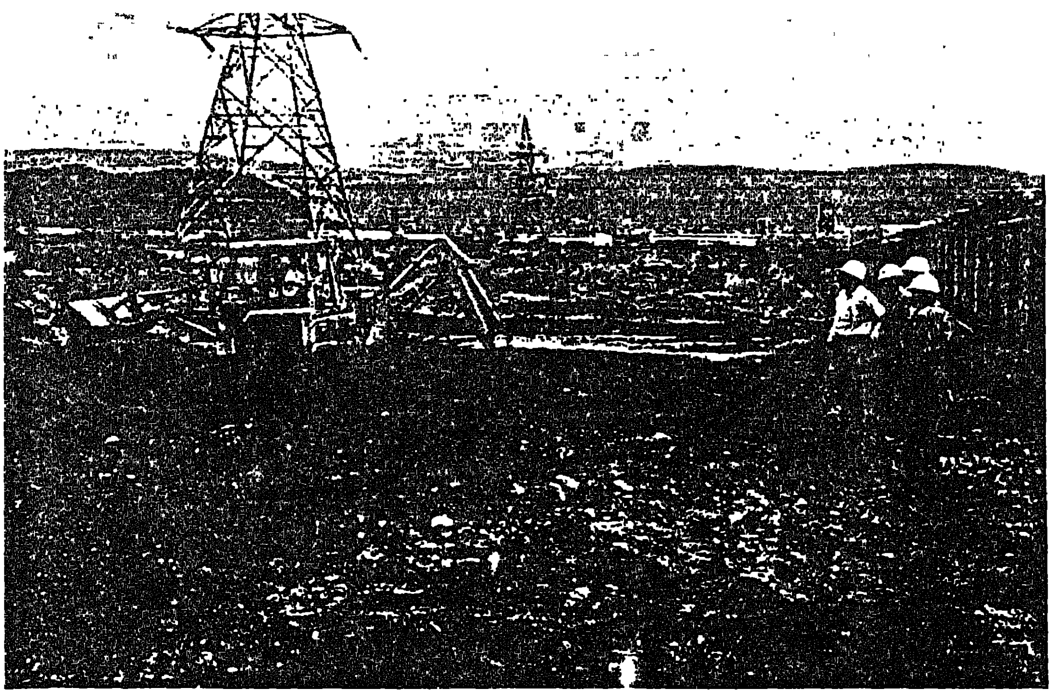


Figure 1 Tilling of sludge after application of Oilzapper on sludge

Oilzapper application on oily sludge at HPCL Refinery, Visakhapatnam

Oilzapper (an oily sludge degrading bacterial system) was produced in a bioreactor at TERI laboratory, New Delhi. After optimum growth of Oilzapper, bacterial cells were mixed with a carrier material. The carrier based Oilzapper (containing 10^8 cells/g carrier material) was filled in sterile polybags (Figure 2) and transported to HPCL Refinery, Visakhapatnam for treatment of oily sludge. In the month of May 2000, first dose of Oilzapper (200 kg Oilzapper) and 200 litres of nutrients were applied on oily sludge. In the month of July 2000, second dose of Oilzapper (150 kg Oilzapper) and nutrients (200 litres) were applied on oily sludge. In the month of September 2000, third dose of Oilzapper (50 kg) and nutrients (100litres) were applied and tilling of sludge was carried at each time of application of Oilzapper by JCB for proper mixing of bacterial cells in sludge.

Monitoring the rate of biodegradation of oily sludge



Figure 2 Oilzapper - oily sludge degrading bacterial system (packet containing live bacteria)

Sludge samples collected from the treatment pit at zero time, after two, four, six and nine months of initiation of bioremediation of oily sludge were transported to TERI laboratory, New Delhi for analysis.

Total petroleum hydrocarbon (TPH) from 10 g sludge samples collected at zero time, after two, four, six and nine months were extracted with hexane, methylene chloride and chloroform (80 ml each) consequently (93-95% extraction efficiency). After extraction, all the three extracts (obtained by hexane, methylene chloride and chloroform) were pooled and dried at room temperature by evaporation of solvents under gentle nitrogen stream in fumehood. After solvent evaporation, the amount of TPH recovered from 10g sludge was determined by simple gravimetry method.

Degradation of various fractions of oily sludge

The TPH recovered from oily sludge at zero time and after two, four, six and nine months were fractionated into alkane, aromatic asphaltene and NSO (nitrogen, oxygen, and sulphur containing compound) with a silica-gel column. The TPH was first dissolved in n-pentane and separated into soluble and insoluble fractions (asphaltenes). The soluble fraction was loaded on silica-gel column and eluted with different solvents. The alkane fraction was eluted with hexane, followed by the aromatic fraction that was eluted with benzene. The NSO fraction was eluted with chloroform and methanol. Alkane and aromatic fractions were concentrated by evaporation of solvents and then 0.2 μl of each was analyzed by gas chromatography (GC –FID Hewlett Packard, 5890 Series II) to identify all the compounds present in the alkane and aromatic fractions. In the alkane fraction, various alkane compounds were identified by matching the retention time with authentic standards. Simultaneously, the identification of each alkane compound was also confirmed by spiking the alkane fraction. A known amount of each standard alkane compound was added to the alkane fraction and injected into GC (co-injection) and the peak area of each alkane compound increased as a result. Similarly, the polycyclic aromatic hydrocarbon compounds were identified by matching the retention time with an authentic standard and confirmed by spiking the sample with authentic standards.

Characterisation of oily sludge

Oily sludge (350 MT sludge) that was biodegraded at HPCL Refinery was characterised before initiation of bioremediation of sludge. Water content in sludge was estimated by sodium sulphate. After removal of water from sludge, oil content (TPH) in sludge was estimated. Oil content was extracted from oily sludge using hexane, methylene chloride and chloroform. After evaporation of solvents, the amount of oil recovered from 10g oily sludge was quantified. The oil (TPH) that was extracted from oily sludge was further fractionated into

alkane, aromatic, asphaltene and NSO (nitrogen, oxygen, sulphur containing compound) with silicagel column. The ash content of oily sludge was estimated after extraction of TPH from sludge. A known amount of residual oily sludge was taken in crucible and heated at 600°C for 5 hours. After cooling, the amount of ash recovered from 10g sludge was quantified by gravimetry.

Analysis of soil of sludge treatment plot

Soil samples were collected from sludge treatment pit at zero time after six and nine months. Soil samples collected at zero time after six and nine months of initiation of treatment were analysed for physico-chemical characterisation of soil.

Analysis of trace metals in soil contaminated with sludge

Various trace metals were analysed from soil samples collected at zero time after nine months. Oily sludge containing soil samples were digested in nitric acid. A known weight of soil was taken in clean 100 ml beaker. A 15 ml concentrated nitric acid was added to beaker and the beaker was covered with a watch glass and heated at 140°C on a hot plate, in a fume hood, until most of the acid was evaporated. The step was repeated thrice in order to solubilise the metallic components. The solution was then filtered in another beaker through 0.45 micron Whatman filter paper number 42 and the insoluble residues on the filter paper was rinsed with 10% nitric acid. The residue was then discarded and beaker was covered with a watch glass and heated at 140°C until complete evaporation of nitric acid. Now the beaker was heated at 400°C until barely dried and white ash appeared. The sample was not allowed to bake and temperature was maintained at 400°C for six hours. The bottom of the watch glass was carefully rinsed into the beaker using 10% nitric acid. The sides of the beaker was also rinsed and solution was evaporated to dryness at 140°C. The filter paper blank and nitric acid blank were also prepared similarly. Each beaker was then cooled and the residue was dissolved in 1 ml of concentrated nitric acid. The clear solution was then quantitatively transferred into 50 ml volumetric flask and volume was made up by using 10% nitric acid. The extract was initially analysed by flame (air-acetylene) AAS using standard method. Some metals such as Se, and As, were analysed by AAS equipped with hydrate system.

3 Results

Physico-chemical properties of soil of soil of bioremediation site

Zero time and after nine months soil analysis showed that texture of soil remained unchanged. At zero time, the water holding capacity of soil was 45.18%, which increased to 57.9% in six and 61.2% in nine months. pH of soil at sludge treatment site remained unchanged even after nine months. However soil bulk density of sludge treatment site increased from 1.15 g/cm^3 to 1.30g/cm^3 in nine months which is comparable to agriculture soil. Organic carbon in soil at sludge treatment site increased from 1.90% to 2.35% in nine months which was due to oily sludge contamination in soil. Available phosphorus in soil also increased 4.6 ppm to 22.4 ppm in nine months. Potassium in soil at treatment site increased from 65 ppm to 74 ppm in nine months . Similarly total nitrogen in soil also increased significantly in nine months. (Table 1).

Table 1 Physical properties of soil of TERI bioremediation site

Test	Zero time	After nine months
Total petroleum hydrocarbon contamination in soil	--	1.6%
PH	7.35	7.38
Soil texture	Red with gravel	Red colour
Water holding capacity of soil	45.18%	61.2%
Soil bulk density	1.15 g/cm^3	1.30 g/cm^3
Organic carbon in soil	1.90%	2.35%
Available phosphorus in soil	4.6 ppm	22.4ppm
Potassium in soil	65 ppm	74 ppm
Total nitrogen in soil	0.08%	0.095%

Selected heavy metals were analysed in soil samples contained oily sludge collected from TERI bioremediation site at zero time after six months and nine months. Concentration of all the heavy metals in soil reduced significantly in nine months. Among nine heavy metals analysed the maximum reduction was of Fe Concentration (Table 2). Concentration of all the heavy metals analysed in soil samples were within the permissible limits.

Table 2 Heavy metal concentration (ppm) in soil samples at bioremediation site

Heavy metal	Concentration (mg/kg soil)		
	At zero time	After six months	After nine months
Fe	30.490	21.4	19.3
Zn	2.642	1.20	1.15
Ni	2.264	0.90	0.90
Cu	5.733	3.40	3.25
Co	0.145	0.09	0.08
Cr	0.325	0.15	0.14
Mn	3.051	0.98	0.99
Pb	1.220	1.20	1.20
Cd	0.025	0.02	0.02

Composition of oily sludge

At zero time (before initiation of bioremediation) composition of oily sludge biodegraded at HPCL refinery was estimated. Water content in sludge was recorded at 17%. Solvent extractable total petroleum hydrocarbon in sludge was 61%, organic matter was 15% and sediment/ash content was 11% (Table 3). TPH recovered from sludge was further fractionated into various fractions which showed 60% alkane fraction, 30% aromatic fraction, 3% NSO fraction and 7% asphaltene fraction (Table 3).

Table 3 Constituents of oily sludge biodegraded at HPCL Refinery

Constituents of oily sludge	Composition (%)
Water	13
Solvent extractable total petroleum hydrocarbon	61
Organic matter	15
Sediment/ash	11
Constituents of TPH	
Alkane fraction	60
Aromatic fraction	30
NSO fraction	3
Asphaltene fraction	7

Bioremediation of oily sludge

A pit contained approximately 350 metric tonnes of oily sludge was selected for bioremediation. In the month of May 2000, Oilzapper (200 kg) and nutrients (200 litres) was applied on oily sludge. At zero time the solvent extractable TPH in oily sludge was recorded 52.81%. Treatment of this sludge with Oilzapper showed that solvent extractable TPH (oil content) in sludge reduced from 52.81% to 23.59% in two months, from 52.81% to 8.33% in four months, from 52.81% to 6.07% in six months and from 52.81% to 1.6% in nine months which revealed 55.33%, 84.2%, 88.5% and 98.8% biodegradation of oily sludge in two, four, six and nine months respectively (Figure 3). Figure 4 shows the sludge pit before and after nine months treatment by Oilzapper.

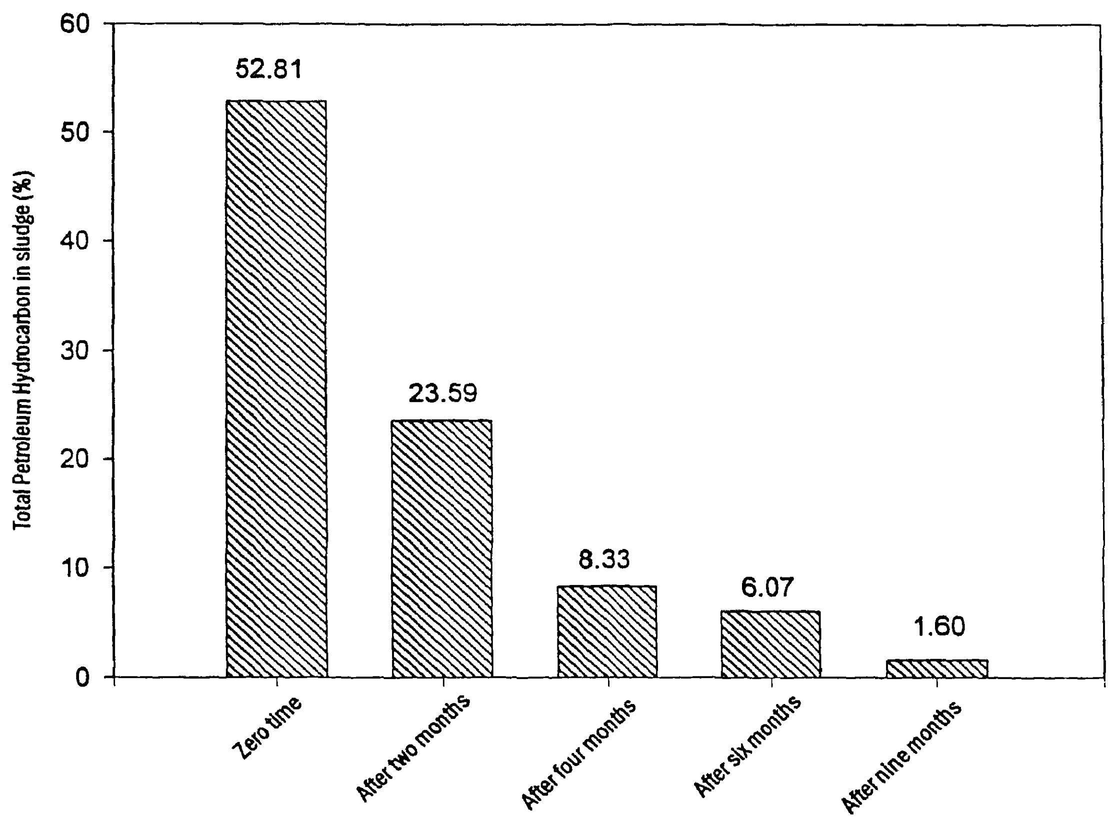
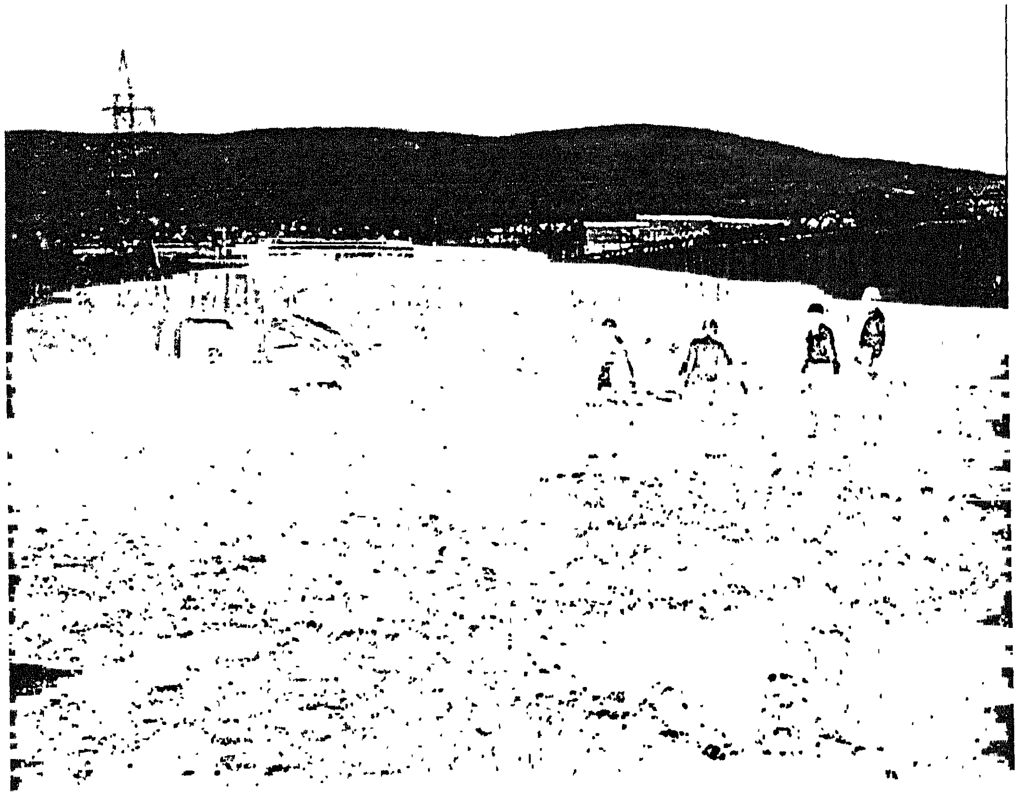


Figure 3 Total tetroleum hydrocarbon oily sludge during bioremediation of oily sludge

Before Treatment



After Treatment



Figure 4 Bioremediation of oily sludge by Oilzapper at HPCL Refinery, Visakhapatnam

Biodegradation of various fractions of oily sludge

Biodegradation of various fractions of oily sludge was estimated. With application of Oilzapper and nutrients, 98.8% oily sludge (total petroleum hydrocarbon) was biodegraded in nine months. Out of 98.8% biodegradation of oily sludge, biodegradation of alkane fraction was accounted for 59.5%, aromatic fraction 29.4% and NSO plus asphaltene fraction 9.9% (Table 4).

Table 4 Biodegradation of various fractions of oily sludge in nine months

Fractions	Biodegradation (%)
Total petroleum hydrocarbon	98.8
Alkane	59.5
Aromatic	29.4
NSO + asphaltene	9.9

GC fingerprinting of biodegradation of alkane and aromatic fractions of oily sludge treated with Oilzapper plus nutrients are shown in Figures 5 and 6 respectively.

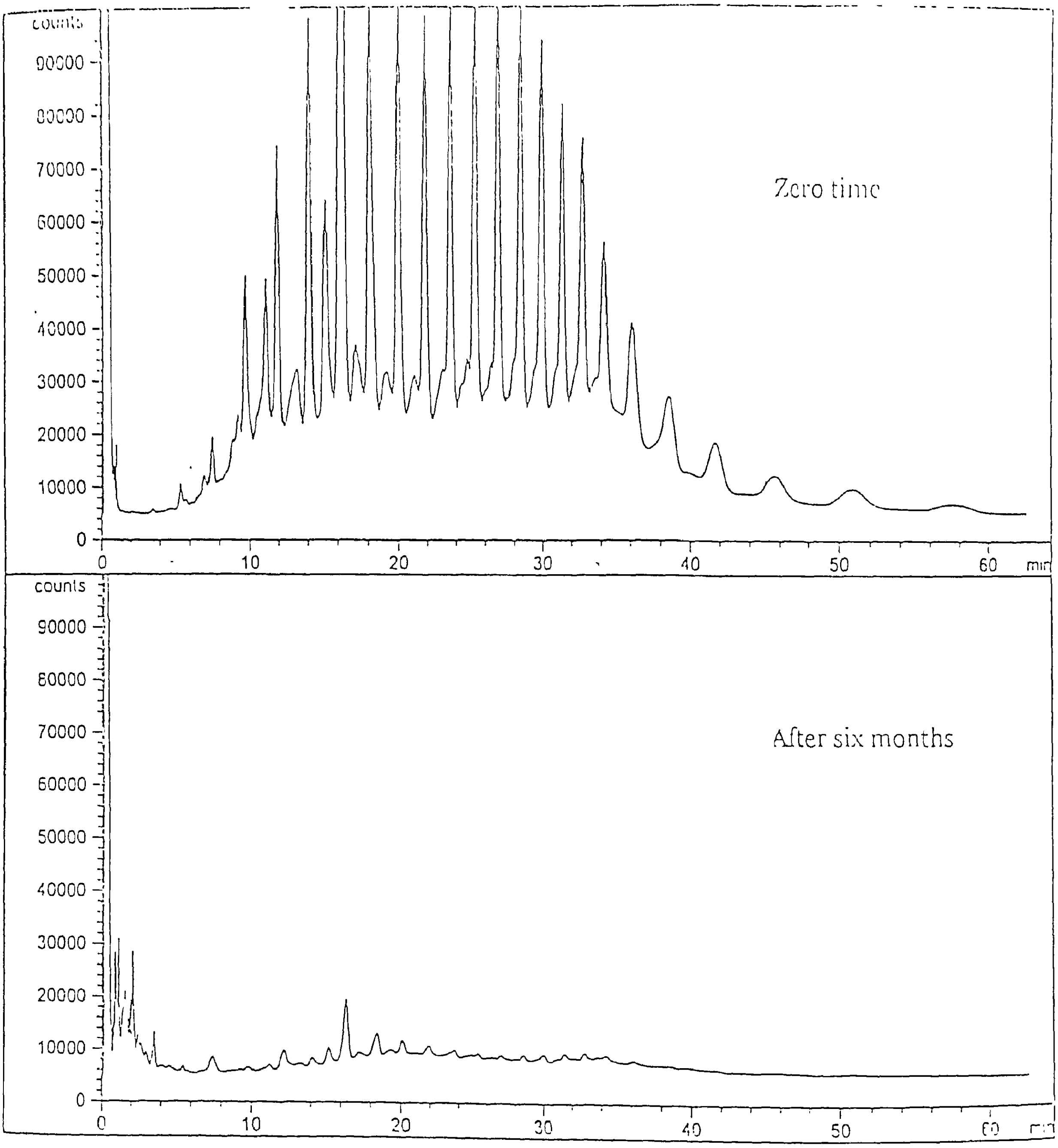


Figure 5 GC fingerprinting of biodegradation of alkane fraction of oily sludge treated with Oilzapper plus nutrients

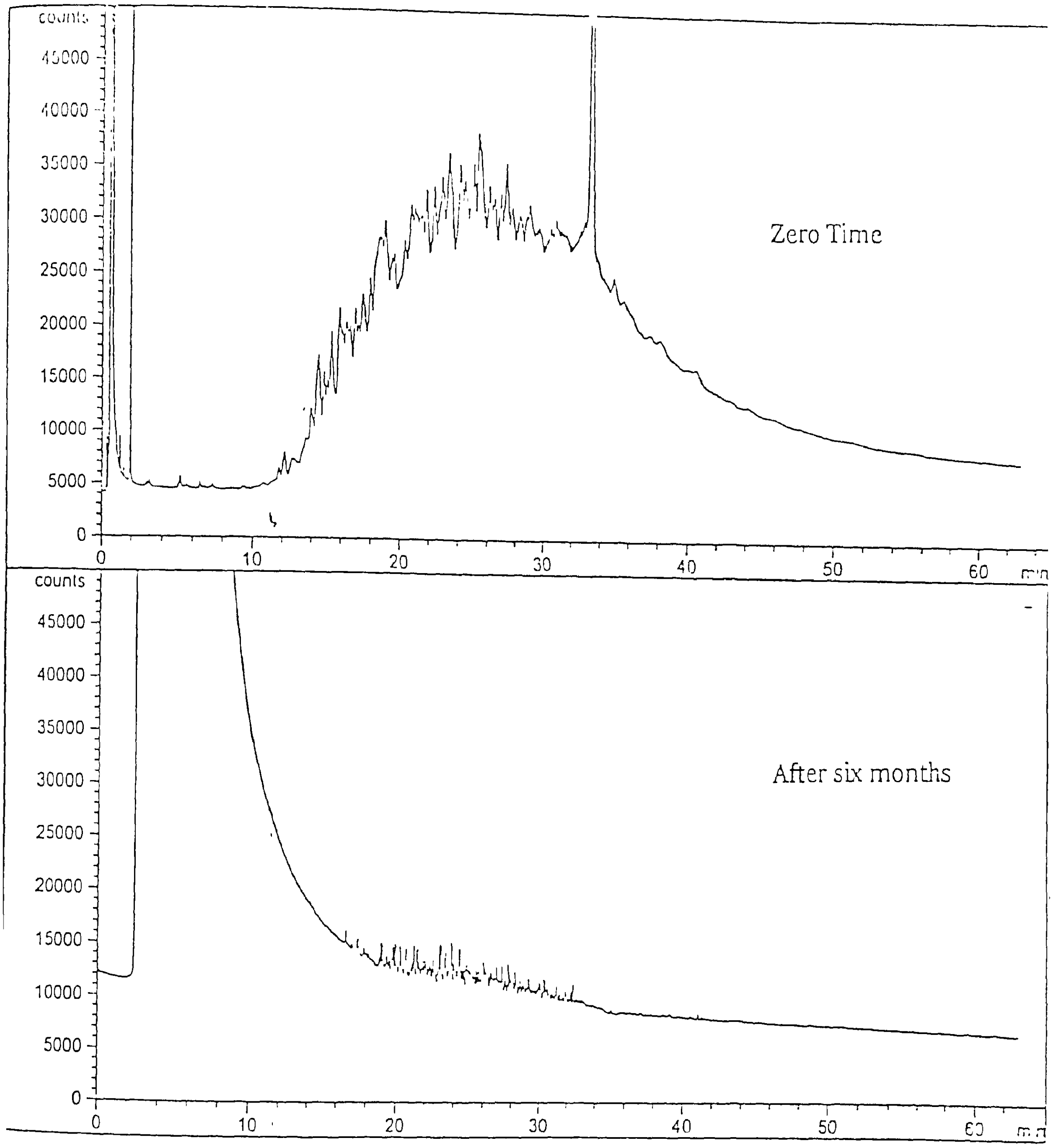


Figure 6 GC fingerprinting of biodegradation of aromatic fraction of oily sludge treated with Oilzapper plus nutrients

4 Summary

- Bioremediation of oily sludge at HPCL Refinery, Visakhapatnam was initiated in the month of May 2000. A pit (approximately 30 m x 20 m) contained more than 350 metric tonnes of oily sludge was undertaken for bioremediation. In the month of May, July and September 2000, Oilzapper and nutrients were applied on oily sludge for biodegradation.
- At zero time (just after application of Oilzapper on sludge), oil content (TPH) in sludge was 52.81%. With application of Oilzapper and nutrients, the oil content in sludge reduced from 52.81% to 1.60% in nine months which revealed 98.8% biodegradation.
- In Oilzapper treated sludge, out of 98.8% biodegradation of TPH in nine months, biodegradation of alkane fraction was accounted for 59.5%, aromatic fraction was 29.4% and NSO plus asphaltane fraction was 9.9%.
- Heavy metals concentration in soil at sludge treatment site reduced significantly in nine months. The concentrations of heavy metals recorded in soil at bioremediation site were within the permissible limits and these concentrations were not having any adverse effect on soil micro-flora and fauna.

5 Recommendations

- Bioremediation of oily sludge at HPCL refinery Visakhapatnam was initiated in the month of February, 2000. Approximately 350 MT oily sludge was undertaken for bioremediation using Oilzapper. Ttreatment of this 350 MT oily sludge with Oilzapper resulted that Oil content in sludge reduced from 52.81% to 1.60% which revealed 98.8% biodegradation of oily sludge. With these increasing results Oilzapper may be used for treatment of oily sludge on regular basis. Treatment of oily sludge by Oilzapper is Eco-friendly and economical viable approach. HPCL Refinery, Visakhapatnam should develop a long-term plan to treat oily sludge by Oilzapper. HPCL Refinery should develop a permanent sludge treatment pit as shown in Figure 7.
- The size of sludge treatment pit may be decided an amount of sludge to be treated. In this pit oily sludge can be treated in batch. In one batch approximately 500 MT oily sludge can be undertaken for treatment which will be biodegraded in two months. Therefore, in one year approximately 2500 MT Oilzapper can treat oily sludge in fine batches. Treated sludge (oil content less than 1%) contained various micronutrient, specially trace element, which are useful for plants growth. Hence treated sludge may be used as manure.
- Oily sludge Management by Oilzapper is a sustainable approach to solve the sludge problem. Therefore, we recommend Oilzapper technology for management of oily sludge at HPCL Refinery, Visakhapatnam.

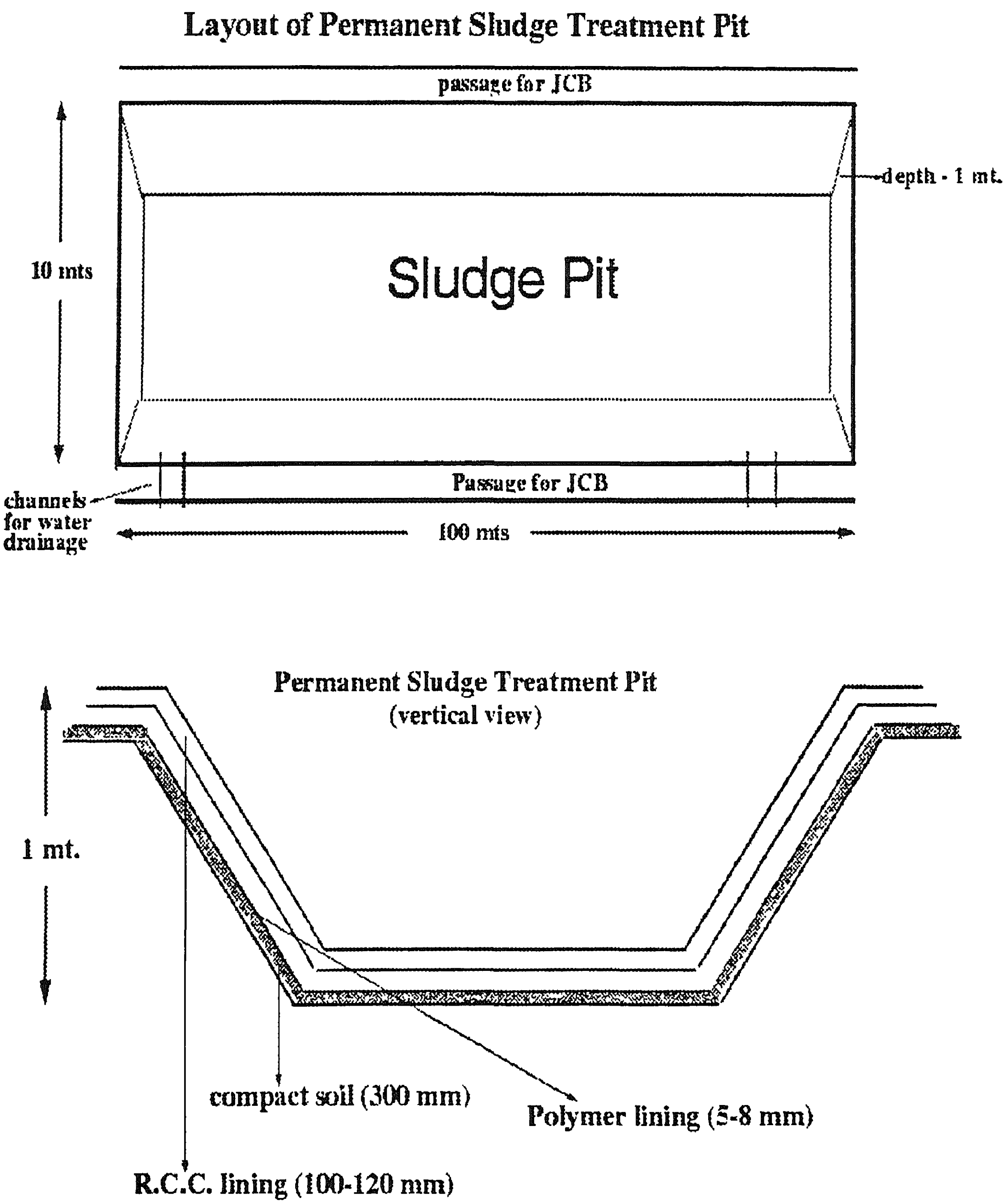


Figure 7 Layout of permanent sludge treatment pit